Synthesis, Electrochemistry, Geometric and Electronic Structure of Oxo-Molybdenum Compounds Involved in an Oxygen Atom Transferring System.

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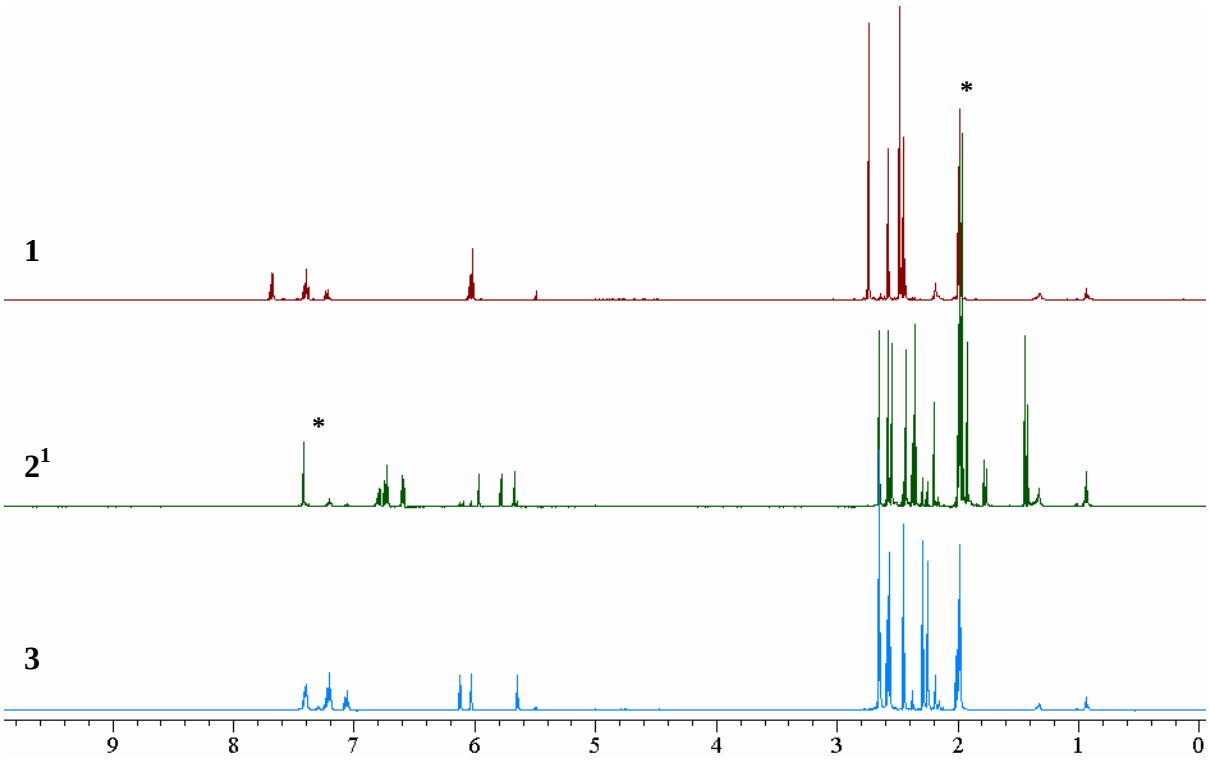
Supporting Information

Figure S1. NMR Spectra of complexes: Tp*MoO_2(SPh), **1** (brown), Tp*MoO(SPh)($OPMe_3$), **2** (green), and Tp*MoO(SPh)(MeCN), **3** (cyan) in acetonitrile-d3 at room temperature.



[1]Additional peaks are due to spontaneous conversion into **3**.
*Solvent peak

Figure S2: Representation of Gaussian fit of a differential pulse voltammetric response of complex Tp*MoO(SPh)($OPMe_3$) with R^2 = 99%, the peak area obtained from the fit used in calculating the change in concentration as a function of time.

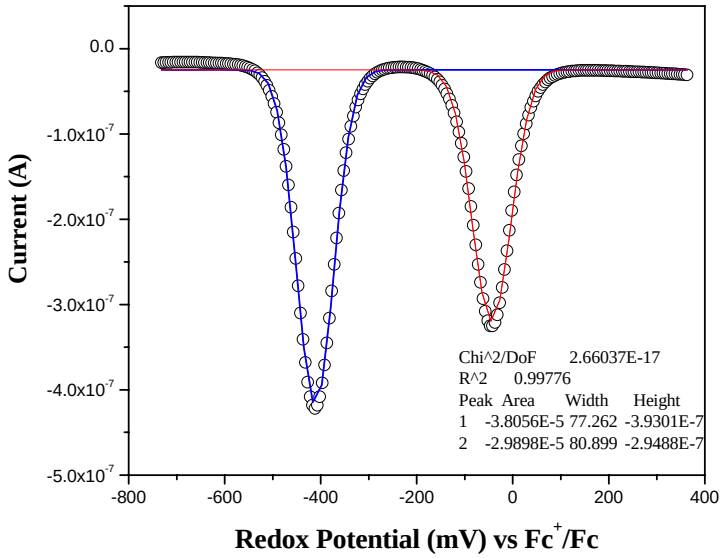


Table 4 Calculated Energies and Orbital Compositions of **1**, **2**, and **3**.

compd	orbital	energy (eV)	orbital contribution %					
1			Mo	Tp*	O1	O2	S	phenyl
	e1 (LUMO+2)	-2.210	68.8	12.1	7.9	7.9	2.1	1.2
	d1 (LUMO+1)	-2.843	67.8	6.9	8.1	9.7	4.3	3.2
	c1 (LUMO)	-3.346	64.7	10.0	8.0	6.0	5.8	5.5
	b1 (HOMO)	**-6.135**	**5.8**	**9.7**	**1.4**	**4.3**	**45.9**	**33.0**
	a1 (HOMO-1)	-6.974	0.1	99.2	0.0	0.1	0.1	0.5
2			Mo	Tp*	O1	$OPMe_3$	S	phenyl
	e2 (LUMO+1)	-1.232	63.4(d_{yz})	16.0	10.8	0.8	5.1	3.9
	d2 (LUMO)	-1.522	65.4(d_{xz})	14.8	11.4	6.8	0.4	1.2
	c2 (HOMO)	**-4.678**	**78.3(d_{xy})**	**9.4**	**0.5**	**3.4**	**4.6**	**3.9**
	b2 (HOMO-1)	-5.412	8.9	7.8	2.7	1.7	45.0	33.9
	a2 (HOMO-2)	-6.420	6.4	49.3	1.3	1.0	25.4	16.6
3			Mo	Tp*	O1	MeCN	S	phenyl
	e3 (LUMO+1)	-1.632	62.9(d_{yz})	14.2	11.0	0.4	5.3	6.2
	d3 (LUMO)	-2.099	54.0(d_{xz})	12.1	12.0	20.8	0.4	0.4
	c3 (HOMO)	**-5.148**	**71.0(d_{xy})**	**11.0**	**1.0**	**4.1**	**8.1**	**4.8**
	b3 (HOMO-1)	-5.791	17.2	9.8	3.2	2.7	43.8	23.3
	a3 (HOMO-2)	-6.375	16.3	7.9	0.8	1.1	46.0	27.9

Calculation Details

Atomic Coordinates used for density functional calculations and basis set used:

Compound 1:

N	0.647	-0.355	7.879
N	1.745	-0.456	7.056
C	2.624	-1.264	7.682
C	2.081	-1.655	8.88
C	0.85	-1.09	8.987
C	3.926	-1.641	7.11
C	-0.161	-1.176	10.084
B	-0.604	0.385	7.39
C	-3.329	-1.083	6.717
N	-0.215	-0.332	4.998
C	-0.857	-0.989	4.015
C	-2.093	-1.375	4.465
C	-2.208	-0.925	5.764
N	-1.061	-0.296	6.078
C	-0.24	-1.221	2.669
N	0.648	2.124	6.117
N	-0.283	1.839	7.097
C	-0.798	2.988	7.573
C	-0.223	4.018	6.893
C	0.672	3.452	5.989
C	1.519	4.165	4.99
C	-1.822	3.028	8.647
O	2.479	-0.929	4.333
Mo	1.791	0.495	4.961
C	4.799	1.871	4.385
C	5.658	2.98	4.463
C	6.535	3.203	3.412
C	6.534	2.433	2.294
C	5.687	1.379	2.242
C	4.816	1.1	3.266
S	3.755	1.594	5.801
O	1.528	1.426	3.567
H	-1.37944	0.34746	8.1551
H	2.54974	-2.29871	9.6096
H	4.52102	-0.74396	6.93865
H	3.77073	-2.16016	6.16424
H	4.45086	-2.2982	7.80334
H	0.27032	-0.78814	11.00684
H	-0.45281	-2.21623	10.22843
H	-1.03798	-0.58636	9.81691
H	-3.5108	-2.14347	6.89152
H	-4.22627	-0.62405	6.30182
H	-3.07564	-0.59786	7.65963
H	-2.83588	-1.92678	3.90816
H	0.67686	-1.79906	2.78435
H	-0.00901	-0.2621	2.20505

H	-0.93913	-1.77056	2.03869
H	-0.42259	5.07069	7.02864
H	2.18424	4.85742	5.50585
H	0.88061	4.71906	4.30183
H	2.11125	3.43967	4.43211
H	-1.42334	2.55937	9.54675
H	-2.7119	2.48972	8.32077
H	-2.08265	4.06429	8.86208
H	5.63601	3.64028	5.31737
H	7.24206	4.01607	3.48544
H	7.19228	2.6559	1.46733
H	5.69637	0.73992	1.37143
H	4.13978	0.26214	3.18165

Basis set
Mo – DGDZVP
N, O, S – 6-311G(d)
H, C, B – 6-31G(d)

Energy, -5701.2112805 Hartee
Method – B3P86

Compound, 2

C	2.791	3.16	5.925
C	6.795	2.521	6.715
N	5.489	0.387	6.527
N	5.279	-0.736	7.314
C	5.93	-0.603	8.483
C	6.564	0.614	8.462
C	6.305	1.195	7.241
C	5.934	-1.661	9.551
O	3.753	0.082	2.906
C	8.413	1.627	1.891
C	5.699	2.201	1.182
C	7.049	3.806	3.12
P	6.829	2.128	2.545
O	6.379	1.19	3.632
Mo	4.506	0.431	4.374
C	6.52	-1.715	2.236
C	6.219	-3.595	3.975
C	5.664	-3.669	5.213
N	5.161	-2.423	5.505
N	5.444	-1.594	4.456
C	6.069	-2.297	3.527
C	5.517	-4.818	6.158
B	4.458	-1.919	6.762
N	2.853	-0.41	5.449
N	3.041	-1.407	6.414
C	1.845	-1.842	6.844
C	0.859	-1.164	6.183
C	1.515	-0.283	5.333
C	1.722	-2.894	7.904
C	0.903	0.694	4.385
S	4.001	2.752	4.744
C	2.012	4.33	5.726
C	1.051	4.702	6.631

C	0.811	4.013	7.759
C	1.558	2.873	7.99
C	2.55	2.476	7.114
H	5.942	3.167	6.507
H	7.361	2.361	5.798
H	7.436	2.993	7.46
H	6.365	-2.579	9.151
H	4.912	-1.851	9.878
H	6.529	-1.32	10.398
H	8.749	2.356	1.153
H	8.318	0.649	1.419
H	9.139	1.57	2.702
H	5.628	1.218	0.716
H	6.058	2.925	0.451
H	4.716	2.505	1.541
H	7.351	4.439	2.286
H	7.82	3.828	3.89
H	6.11	4.174	3.535
H	6.044	-2.246	1.412
H	7.603	-1.811	2.153
H	6.244	-0.661	2.196
H	6.692	-4.404	3.438
H	6.503	-5.206	6.414
H	4.929	-5.604	5.685
H	5.012	-4.481	7.063
H	4.377	-2.727	7.489
H	-0.208	-1.288	6.298
H	2.2	-2.545	8.819
H	2.209	-3.809	7.566
H	0.668	-3.093	8.097
H	1.219	0.46	3.368
H	1.226	1.702	4.643
H	-0.183	0.633	4.451
H	2.179	4.937	4.848
H	0.463	5.585	6.429
H	0.059	4.339	8.462
H	1.362	2.281	8.872
H	3.153	1.614	7.357
H	7.158	1.038	9.258

Basis set
Mo – DGDZVP
N, O, S – 6-311G(d)
H, C, B, P – 6-31G(d)

Energy, -6163.1684509 Hartee
Method – B3P86

Compound, 3

N	0.294	2.686	2.869
S	-0.744	3.94	0.186
O	1.91	2.147	0.51
Mo	1.388	3.543	1.263
N	2.373	4.865	-0.072
N	3.267	5.879	0.352
C	3.797	6.461	-0.676

C	3.293	5.923	-1.855
C	2.43	4.95	-1.442
C	1.675	4.026	-2.225
C	4.785	7.622	-0.574
N	3.228	3.657	2.466
N	3.98	4.791	2.518
C	5.076	4.529	3.262
C	5.055	3.271	3.644
C	3.881	2.727	3.147
C	3.333	1.316	3.33
C	6.095	5.619	3.551
N	1.101	5.607	2.49
N	2.177	6.496	2.492
C	1.82	7.618	3.157
C	0.538	7.497	3.533
C	0.097	6.242	3.094
C	-1.217	5.654	3.317
C	2.785	8.783	3.314
B	3.52	6.093	1.844
H	4.059	7.13	1.939
C	-2.821	0.634	1.231
C	-1.846	1.48	0.765
C	-1.986	2.859	0.84
C	-3.172	3.34	1.368
C	-4.168	2.539	1.827
C	-3.995	1.138	1.792
C	-0.353	2.264	3.722
C	-1.158	1.783	4.804
H	-0.859	2.179	5.673
H	-1.061	0.788	4.841
H	-2.116	2.018	4.643
H	-3.307	4.33	1.412
H	-5.002	2.947	2.199
H	-4.708	0.532	2.145
H	-2.669	-0.354	1.201
H	-1.024	1.101	0.339
H	3.530827	6.210299	-2.868557
H	2.353679	3.411441	-2.816448
H	1.007723	4.573859	-2.890351
H	1.08697	3.387016	-1.566198
H	5.664759	7.302419	-0.01543808
H	4.311488	8.457856	-0.05899417
H	5.083581	7.933985	-1.574807
H	5.805451	2.761444	4.230154
H	3.180161	1.120396	4.391357
H	4.043825	0.5949711	2.926336
H	2.383253	1.223919	2.803121
H	5.611022	6.436321	4.085651
H	6.504915	5.991326	2.612148
H	6.899863	5.211059	4.162457
H	-0.04438496	8.229218	4.072523
H	-1.981109	6.294198	2.87611
H	-1.395788	5.559623	4.388087
H	-1.257294	4.668201	2.853667
H	3.069091	9.154686	2.329499
H	3.675077	8.448253	3.846736

H	2.302432	9.580997	3.878295

Basis set
Mo – DGDZVP
N, O, S – 6-311G(d)
H, C, B – 6-31G(d)
Energy,-5758.9417985 Hartee
Method – B3P86